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De kristalstructuur van P4S10 en P4S7

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SUMMARY

In the introduction a survey of some of the properties and applications of the phosphorus sulfides is given. From this it appears that very little was known with certainty about the structures of these compounds. Therefore an X-ray diffraction study of these sulfides was undertaken. The structure determinations of P_4S_{10} and P_4S_7 are described.

P_4S_{10} belongs to the space group $P\bar{1}$. The lattice parameters were determined by combining the information from optical goniometric measurements with that obtained from oscillation and Weissenberg photographs about the a axis. The following values were obtained:

$$\begin{aligned}a &= 9.07 \text{ \AA}, b = 9.18 \text{ \AA}, c = 9.19 \text{ \AA}; \\ \alpha &= 92^\circ.4, \beta = 101^\circ.2, \gamma = 110^\circ.5;\end{aligned}$$

two molecules per unit cell.

The intensities of most reflexions hkl were measured from integrated oscillation photographs about the a axis. With the F^2 values obtained, a three-dimensional Patterson synthesis was computed. In this vector map the origin was surrounded tetrahedrally by four independent high peaks at a distance of about 2 Å. This indicated the presence of PS_4 tetrahedra in a parallel or centrosymmetric orientation. Starting from this information and combining further information from the Patterson synthesis with chemical evidence, the structure was shown to consist of molecules P_4S_{10} (fig. 9). Two such molecules are centrosymmetrically arranged in the unit cell. Their orientation was found from the vector map, their approximate position relative to the centre of symmetry by trial and error, making use of the reflexions $h00$, $0k0$ and $00l$. The coordinates were refined by computing successive Fourier syntheses of the $[100]$ and $[010]$ projections. The procedure followed for the $[010]$ projection is schematically shown in table III. The final atomic coordinates (table VII) were corrected for the finite-series effect by Booth's backshift method. The values attained for the disagreement indices were 0.11, 0.11 and 0.12 for the observed $0kl$, $h0l$ and $hk0$ reflexions respectively. The temperature factor was found to be $\exp(-2.36 \sin^2 \theta / \lambda^2)$.

For P_4S_7 , which belongs to the space group $P2_1/n$, the following lattice parameters were obtained from oscillation, rotation and Weissenberg photographs about the three crystal axes:

$$a = 8.87 \text{ \AA}, b = 17.35 \text{ \AA}, c = 6.83 \text{ \AA}, \beta = 92^\circ.7;$$

four molecules per unit cell.

The intensities of most reflexions hkl were obtained from integrated equi-inclination Weissenberg photographs about the c axis. After some unsuccessful applications of phase relationships between the structure factors $0kl$ and $hk0$ respectively, a three-dimensional Patterson synthesis was computed. For the interpretation of this synthesis the Harker section and the Harker line were particularly useful. The "non-Harker maxima" in the section $(x, \frac{1}{2}, z)$ were eliminated by combining the information from this section with that obtained from the zero section and by trial and error on the reflexions $h0l$ with h and l even. Making use of the position of the maxima around the origin, the Harker maxima and some general peaks in the Patterson synthesis, and combining this information with chemical arguments, the approximate structure was determined. The general shape of the molecule, which is shown in fig. 28, does not correspond to any of the structures suggested for P_4S_7 previously. The atomic coordinates were refined by successive Fourier syntheses of the three projections. The final atomic coordinates (table ix) were corrected for the finite-series effect by the backshift method. The final values of the disagreement indices for the observed $0kl$, $h0l$ and $hk0$ reflexions amount to 0.08, 0.13 and 0.10 respectively. The temperature factor was found to be $\exp(-2.47 \sin^2 \theta / \lambda^2)$.

In both crystal structures the molecules are separated by shortest intermolecular distances of 3.4 Å. The P-P distance in P_4S_7 is remarkably large, namely 2.37 Å with an estimated standard deviation of 0.04 Å. As was shown by the " χ^2 -test" (a many-parameter significance test), which is discussed in some detail in the appendix, only two types of P-S bonds may be distinguished in both molecules. The values for the mean bond lengths are 1.95₃ and 2.08₂ Å with estimated standard deviations of 0.012 and 0.007 Å respectively. The bond lengths are compared with distances known from other structures in chapter III, section 6.

In P_4S_{10} the S-P-S and P-S-P angles show no significant deviation from 109°.5. In P_4S_7 the PS_4 tetrahedra are distorted, since the deviation of some S-P-S angles from 109°.5 is larger than 2.5 times the standard deviation. The mutual differences between the individual bond lengths and angles of the same type do not indicate a significant deviation from a symmetry $\bar{4}3m$ and $mm2$ for the P_4S_{10} and P_4S_7 molecules respectively.

In the appendix a discussion is given of the errors in the atomic coordinates obtained from Fourier syntheses. For the [001] projection of P_4S_7 imperfect correction for the finite-series effect appeared to increase the standard deviation in the atomic coordinates by approximately 0.002 Å.